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**Current Progress on the Study of Model,
Polystyrene-Based, Polymer-Layered
Silicate Nanocomposites**

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Current Progress on the Study of Model, Polystyrene-Based, Polymer-Layered Silicate Nanocomposites

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1. Introduction

Composites from polymers and layered silicate clay minerals have been an intriguing area of research for over a decade [1]. Exciting initial results with these systems gave strength to the notion that reinforcing soft materials with a nanoscopic filler particle could vastly alter and improve the physical properties of these materials [2, 3]. These new materials immediately found application in high-temperature automotive environments based on the work at Toyota. These materials gain added importance when compared to existing technology, which falls well short of the needs of the Objective Force Warrior. The soldier needs new materials capable of addressing a variety of pressing needs, from traditional ballistic threats to newer needs such as protection from chemical and biological warfare agents, lightweight power supplies, and a general reduction in weight that the soldier currently carries into battle. Polymer-layered silicate nanocomposite (PLSN) may provide solutions to some of these needs.

During the years following the reports by Kojima et al. [2, 3], a critical gap in understanding the behavior of PLSNs has emerged. Most methods for fabricating PLS nanocomposites rely on very direct methods for achieving mixing, such as *in situ* polymerization or extrusion with high shearing [1]. Mixing the clay and monomer during polymerization makes penetration of the clay galleries easier, but only works for systems where the polymer can be made simply, in the presence of the clay. *In situ* polymerization also alters the molecular structure of polymers from that which they would have when polymerized in the absence of clay. This limits the usefulness of this technique when considering polymer matrices that have been specifically designed to have special properties. Melt intercalation, with the aid of an extruder, physically destroys the clay tactoids by the application of great shearing forces. This process can lower the particle size of the individual clay platelets and can degrade the polymer—again, a limitation when using specifically designed materials. Both of these processes completely ignore any thermodynamic interactions between the components even though it is these thermodynamic interactions that govern, at the most basic level, the morphology and properties of these materials. While in some cases it is possible to work around the lack of understanding of these interactions [4], it usually prohibits the development and use of nanocomposites from the most interesting polymers.

In 1998, Balazs et al. developed a mean-field model that addresses these fundamental thermodynamic interactions [5]. The model uses Flory-Huggins-type (χ) potentials to consider the enthalpic interactions between the polymer matrix, silicate surface, and a short chain surfactant used to modify the surface of the clay. Free energy density is given as a function of gallery height, allowing the determination of the predicted equilibrium morphology. Balazs et al. calculate the free energy behavior for several different situations, including variations in homopolymer-surfactant enthalpic interactions, variations in surfactant length, and variations in surfactant density on the silicate surface. Other parameters, such as homopolymer-silicate

interaction and affinity of the cation head group on the surfactant are included in the model but not examined. A wide range of behaviors, from phase separation to exfoliation, depend on the specific inputs. However, of note is the prediction that even a nanocomposite in which the polymer and surfactant have no enthalpic affinity or repulsion ($\chi = 0$), intercalation, and exfoliation can occur. This has not been observed experimentally.

In this work, several series of samples have been fabricated to test different aspects of the Balazs model. Variations in the surfactant length and surfactant coverage of the silicate surface are being considered. The mechanical properties of these materials have also begun to be explored. Some of these results have been published elsewhere. This technical note will describe recent developments and work currently underway [6].

2. Experimental

The preparation of the samples for this work has been described in part elsewhere [6]. Wyoming montmorillonite (SWy-2) was purchased from the Missouri Clay Repository. The primary cation present in the as-received material is Na. The clay was cleaned by dispersing in water and then centrifuging to separate the clay from the heavier impurities such as Fe_2O_3 . The clay was then dried and ground into a powder. The cation exchange capacity of the SWy-2 montmorillonite was given as 76.4 meq/100 g (pH unstated), but was measured at pH 7.0 to be 66.7 meq/100 g. The surface area of the clay is assumed to be $\sim 800 \text{ m}^2/\text{g}$ [7].

A series of polystyrene (PS)-based, quaternary-amine terminated surfactants have been synthesized via living anionic polymerization by a procedure described elsewhere [8]. Five surfactants were synthesized, spanning a range of molecular weights from 1700 to 18,000 g/mol. Precise details of the surfactant compositions are given in Table 1. These surfactants are inserted into the montmorillonite via a simple cation exchange reaction in acetone. The modified clays are mixed, by hand and at room temperature, with homopolymer PS, ensuring that little shearing force is added to any system that might change the morphology from equilibrium. The mixture is then pressed into a pellet with minimal pressure and annealed under vacuum at 130°C for a minimum of 1 week.

Table 1. Molecular characteristics of PS-based surfactants, as determined by gel permeation chromatography of the unquaternized materials.

Surfactant Name	M_n (g/mol)	PDI (M_w/M_n)
QPSt-16	1735	1.05
QPSt-15	2700	1.04
QPSt-14	6800	1.03
QPSt-19	11,200	1.04
QPSt-20	17,600	1.03

Three series of samples were fabricated. The first series consisted of PS homopolymer with ~5 weight-percent (mineral content) clay, where the clay was modified as fully as possible with surfactant. The second series was composed of PS homopolymer with ~5 weight-percent (mineral content) clay, where the clay was modified only partially with surfactant. The surfactant was exchanged to a level of 17% of the available exchange sites. The third series of samples was made of PS homopolymer and ~5 weight-percent clay (mineral content), where the clay was modified to 17% with the longer 4 of the 5 surfactants, and then to 83% with the shortest surfactant. For all materials, the PS homopolymer was of low polydispersity and molecular weight of 10,000 g/mol.

The morphology was characterized using small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). X-rays were generated by a Rigaku Ultrax18 rotating anode with Cu cup, and monochromated using a pyrolytic graphite crystal mounted directly to the generator housing. SAXS was performed using an Anton-Paar HR-PRK camera modified with a custom built 200- μ m pinhole with a kinematic mount from Molecular Metrology, located at the monochromator. The data were collected using a BrukerAXS Hi-Star area detector and analyzed using the accompanying GADDS software. TEM was performed with a JEOL 200CX microscope operated at 200-kV accelerating voltage. Samples were microtomed using a Microstar diamond knife and a Leica UCT ultracryomicrotome. Section thickness was ~50 nm.

3. Results and Discussion

The results for the first series of samples have been published elsewhere [6]. In brief, it was found that only phase-separated morphologies occurred after annealing the samples, despite calculations showing that adequate time was allowed for diffusion of the PS homopolymer into the clay galleries. Further examination revealed that, based on the theories of Leibler, autophobic dewetting of the homopolymer from a densely packed surfactant brush appeared to be most likely [9, 10]. In the SAXS data, some of which is shown in Figure 1, there were no differences observed between the modified clay and from the nanocomposite material after annealing, indicating that a phase separated morphology was formed. This behavior was found to be in qualitative agreement with the Balazs model, which indicated that as surfactant coverage (density) on the silicate surface increased, the likelihood of intercalation decreased. The coverages for the first series of samples were all considerably higher than those values used in the model calculations.

Figure 2 shows SAXS data collected for the samples in the third series fabricated—where two surfactant lengths are used to create a brush that shields the homopolymer from the silicate surface— but has long chains to provide a reduction in the entropic penalty to the intercalating homopolymer. As in Figure 1, one can see that there is minimal change in the data, which indicates that there is also no change in the structure of the clay tactoids after annealing.

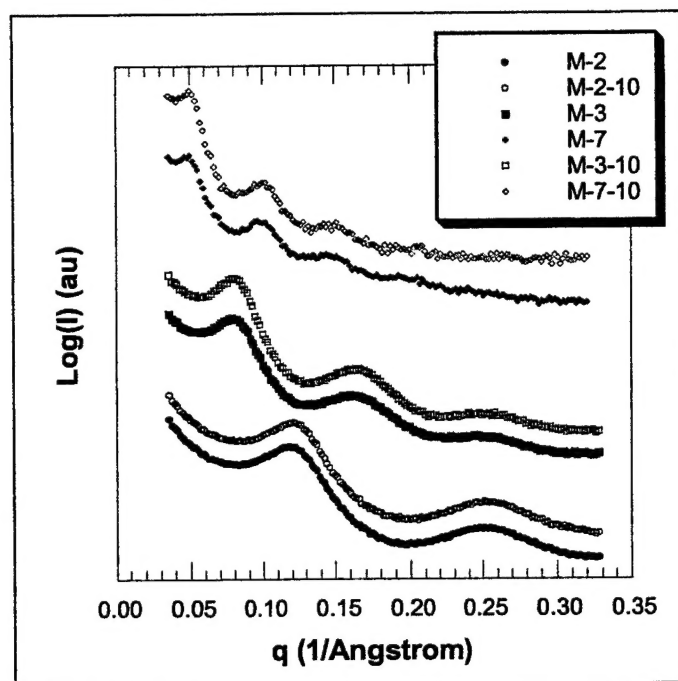


Figure 1. SAXS data for modified clays and PLSNs made from those clays, showing no change in structure upon fabrication of the PLSN.

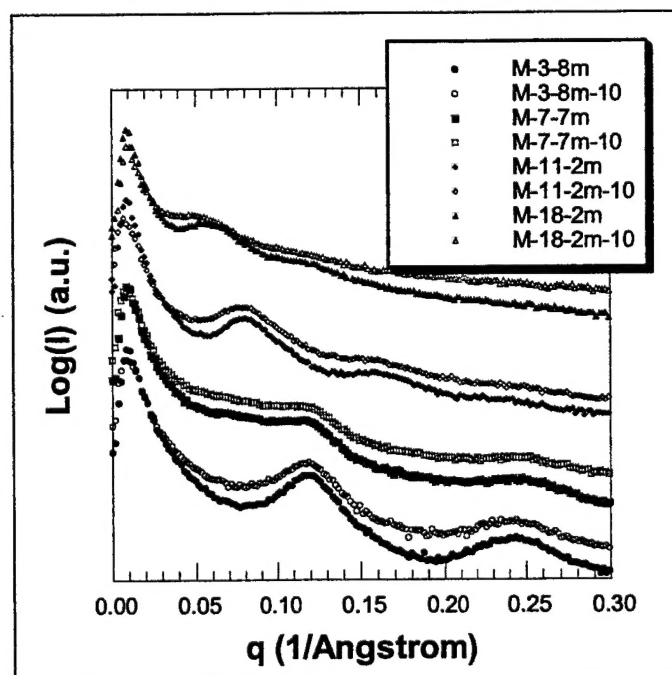


Figure 2. SAXS data for the third series, where the clay was modified with both long and short surfactant chains.

This would only occur if the homopolymer matrix and clay tactoids are phase separated. Although this brush structure is very similar to that shown in other work to increase the ability of a homopolymer melt to wet a polymer brush [11], one can see that in these samples that is not the case.

Figures 3 and 4 show the SAXS data collected for the second series of samples, in which the montmorillonite clay is covered only partially with surfactant, ~17%. These samples were fabricated to closely match the coverage parameters used by Balazs et al. in their calculations. Figure 3 shows the data collected for the samples made using the two longest surfactants, M-11-2p-10 and M-18-2p-10. Clearly, again, one finds only phase-separated morphologies being formed despite the relatively low density of the polymer brushes. However, this is not the case for the SAXS data shown in Figure 4. For these three sets of samples, one can see clearly that a different morphological behavior is evident. In the case of samples M-7-7p-10 and M-2-8p-10, a general lack of features is the cause for interest. As in all previous samples, Bragg reflections are expected. (See Figure 1 for an example.) Bragg reflections indicate ordered structure, and the intensity and number of reflections give evidence of the range of the ordering. Here, however, we see little evidence of order. There is little evidence of a change in morphology, while TEM work confirms the presence of clay in the sample. Figure 5 shows a representative micrograph from sample M-7-7p-10. While clay is clearly evident in the sample, the relative disorder is likely the cause of the lack of Bragg reflections in SAXS. The question remains why the clay would be disordered after modification with the surfactant, especially given the previous ease with which materials were made for sample series 1 and 3.

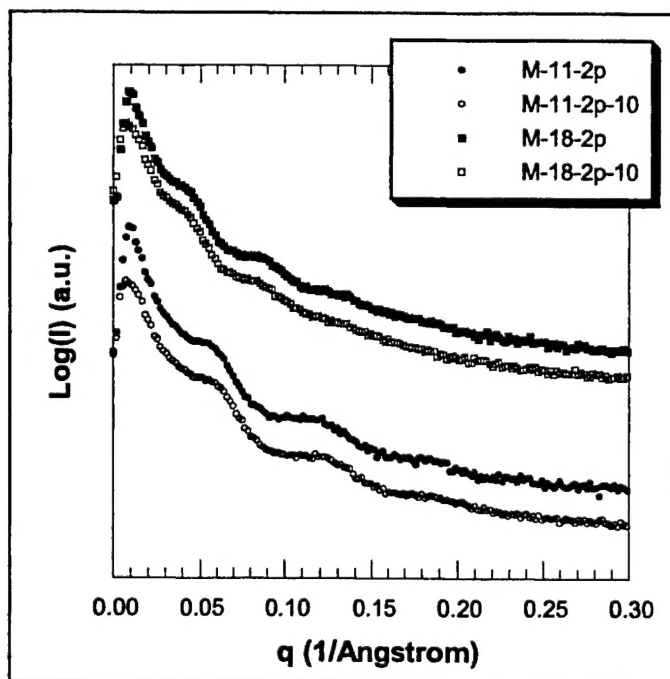


Figure 3. SAXS data for clays modified partially with surfactants Q19 and Q20, and PLSNs made from those clays, showing no evidence of intercalation.

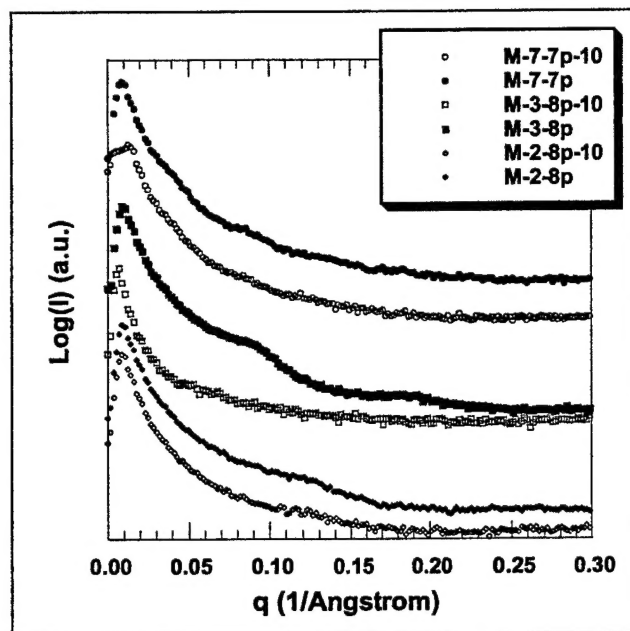


Figure 4. SAXS data for partially modified clays and corresponding PLSNs. Sample M-3-8p-10 shows a marked change in scattering, indicative of intercalation of the homopolymer into the clay galleries.

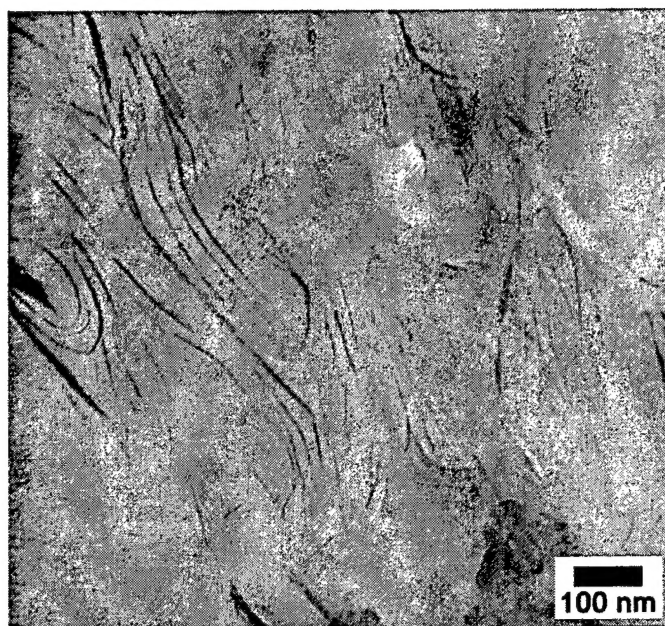


Figure 5. Representative micrograph from sample M-7-7p-10. The modified clay shows an unusual lack of Bragg reflections from the clay by itself, and also from the PLSN. Clay layers are clearly visible and significantly disordered. Currently, work is underway to reproduce the starting materials for this sample and to confirm the quaternization of the surfactant.

The data collected for sample M-3-8p-10 are the most promising. In this case, an ordered sample with clear but weak Bragg reflections becomes disordered after blending and annealing with PS homopolymer. This is what would be expected if melt intercalation had occurred. TEM of the sample has not produced conclusive evidence to date. However, if confirmed, such behavior would be the first observation of direct, equilibrium melt intercalation of a hydrophobic polymer into a hydrophilic clay, and a confirmation of the predictions of the Balazs model. Samples are currently being prepared to confirm or contradict these observations, including returning to the quaternization step in the production of the PS-based surfactants. The absence of any Bragg reflections in the modified clay sample M-7-7p are most dubious and may indicate some anomaly in the functionalization process that could have subsequently affected morphology.

One factor not considered by the model or these specific experiments is the role of the silicate surface in this direct melt intercalation process. It has been suggested that an attractive force exists between polystyrene-like molecules and the hydrophilic silicate surface [12]. This would explain these results, and contradict the model calculations, which were done with no attractive force between surface and homopolymer. Experiments are currently underway to ascertain the extent of this effect.

Finally, efforts are underway to measure the mechanical properties of these materials, now that evidence of changing morphological behavior has been found. These measurements are being conducted through a variety of techniques, including micro- and nanoindentation rheology, using a very small parallel plate cell, and dynamic mechanical analysis. These techniques were all selected for their ability to measure properties where sample size is severely limited.

4. Conclusions

Three series of samples designed to test the predictions of the Balazs model for the role of thermodynamic interactions in determining morphology in PLSNs were synthesized and characterized. Fully modified clay produced only a phase-separated morphology. Partially modified clay produced morphologies that may be indicative of equilibrium homopolymer intercalation. Clays modified with mixtures of surfactants produced only phase-separated morphologies. Evidence of a change in morphology based only on annealing a modified clay in the presence of homopolymer appears to confirm the predictions of the Balazs model, which states that a homopolymer may still intercalate a layered silicate gallery even if there is no enthalpic driving force between the surfactant and homopolymer. The role of the silicate surface-homopolymer interactions is being considered currently, as well as the effects of these morphological changes on mechanical properties.

5. References

1. Giannelis, E. P. "Polymer Layered Silicate Nanocomposites." *Advanced Materials*, vol. 8, p. 29, 1996.
2. Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito. "Mechanical-Properties of Nylon 6-Clay Hybrid." *Journal of Materials Research*, vol. 8, p. 1185, 1993.
3. Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito. "Sorption of Water in Nylon-6 Clay Hybrid." *Journal of Applied Polymer Science*, vol. 49, p. 1259, 1993.
4. Aranda, P., and E. Ruiz-Hitzky. "Poly(ethylene oxide)/NH₄⁺-smectite Nanocomposites." *Applied Clay Science*, vol. 15, p. 119, 1999.
5. Balazs, A. C., C. Singh, and E. Zhulina. "Modeling the Interactions Between Polymers and Clay Surfaces Through Self-Consistent Field Theory." *Macromolecules*, vol. 31, p. 8370, 1998.
6. Beyer, F. L., N. C. Beck Tan, A. Dasgupta, and M. E. Galvin. "Morphological Behavior of Model Polymer-Layered Silicate Nanocomposites." *Chemistry of Materials*, vol. 14, p. 2983, 2002.
7. Van Olphen, H., and J. J. Fripiat. *Data Handbook for Clay Materials and Other Non-Metallic Minerals*. New York: Pergamon Press, p. 346, 1979.
8. Quirk, R. P., and Y. Lee. "Quantitative Amine Functionalization of Polymeric Organolithium Compounds With 3-Dimethylaminopropyl Chloride in the Presence of Lithium Chloride." *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 38, p. 145, 2000.
9. Leibler, L., and A. Mourran. "Wetting on Grafted Polymer Films." *MRS Bulletin*, vol. 22, p. 33, 1997.
10. Ferreira, P. G., A. Ajdari, and L. Leibler. "Scaling Law for Entropic Effects at Interfaces Between Grafted Layers and Polymer Melts." *Macromolecules*, vol. 31, p. 3994, 1998.
11. Reiter, G., J. Schultz, P. Auroy, and L. Auvray. "Improving Adhesion Via Connector Polymers to Stabilize Non-Wetting Liquid Films." *Europhysics Letters*, vol. 33, p. 29, 1996.
12. Vaia, R. A., and E. P. Giannelis. "Polymer Melt Intercalation in Organically Modified Layered Silicates: Model Predictions and Experiment." *Macromolecules*, vol. 30, p. 8000, 1997.

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